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Aqueous-phase hydrodeoxygenation of propanoic acid over the Ru/ZrO_2 and $Ru-Mo/ZrO_2$ catalysts

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ABSTRACT

The conversion of propanoic acid under high hydrogen pressure has been studied over zirconia-supported monometallic Ru and bimetallic Ru–Mo catalysts. The cleavage of C–C bond of propanoic acid to methane and ethane is improved and the formation of C=O hydrogenation products (propanol and propane) is decreased with increasing the temperature. Upon addition of Mo, both the overall activity and the C–C bond cleavage selectivity decrease while the selectivity of C=O hydrogenation increases. With increase of Mo contents, the C–C bond cleavage reaction is significantly inhibited, especially at high temperature. This is also confirmed by the DRIFTS of propanoic acid, showing that the propanoyl intermediate species on Ru–Mo bimetal catalysts is more difficult to dissociate to CO compared with Ru monometal catalyst. Based on H₂-TPR, CO-FTIR and DRIFTS of propanoic acid characterizations, the reaction mechanisms and the resulting selectivity towards the possible reaction paths (C–C bond cleavage/C=O hydrogenation) are discussed in terms of the formation of Ru–MoO_x and the stability and variety of propanoyl intermediate species and the formation of Ru–MoO_x interface are the important factors for the decrease in the TOF of propanoic acid and the C–C bond cleavage selectivity.

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1. Introduction

Biomass is a renewable feedstock that can be used for the production of fuels and chemicals. The transformation of biomass feedstocks to fuels or chemicals primarily calls for the decrease in the effective oxygen to carbon molar ratio [1]. The aqueousphase hydrodeoxygenation (APHDO) reactions [2–17] are a crucial component of a number of strategies for the conversion of biomassderived feedstocks into fuels and chemicals, e.g., hydrogenation of targeted functionalities of biomass including acids, sugars, aldehydes and furans. Typically, most of works have been performed by Dumesic, Miller and Jackson's groups [2–9,16,18,19], i.e., alcohol production from organic acids [2,8], gasoline production from biooils [18], and alkane production from carbohydrates [4,7,16,19].

Among the feedstock bio-chemicals, organic acids and polyols are important platform molecules. The APHDO of carboxylic acids to alcohols has been investigated as a possible pathway for production of novel, high-valued products from bio-derived feedstock

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[20]. The direct APHDO of organic acids offers an alternative that is atom economical and amenable to continuous processing, and that obviates the need for intermediate esterification, use of organic solvents, and byproduct waste streams [20]. In recent work [21], we have studied APHDO of propanoic acid served as a probe reaction over supported Ru catalysts. The results presented that the C=O hydrogenation route of propanoic acid gave the propanol and propane products, the C-C bond cleavage route gave the equimolar amounts of methane and ethane products. It is found that the reaction routes strongly depend on the nature of support. Specially, the Ru/C and Ru/ZrO₂ catalysts exhibited excellent activity for conversion of propanoic acid. However, the cleavage of C-C bond adjacent to the oxygen atom is dominant reaction at high temperature. Therefore, it is desirable to obtain the catalysts that exhibit high activities and high selectivities for APHDO of biomass feedstocks.

In this work, the APHDO of propanoic acid served as a probe reaction was studied over Ru/ZrO_2 and $Ru-Mo/ZrO_2$ catalysts in order to study the effect of Mo promoter on catalytic activity and reaction routes (C–C bond cleavage and C=O hydrogenation). The catalysts were characterized by N₂-physisorption, CO pulse chemisorption, H₂-TPR, H₂-TPD, CO-FTIR and DRIFTS of propanoic acid to provide insight into the effect of Mo additives. The results from this paper suggested that the APHDO reaction can be tuned to make a

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